MATERIALS SCIENCE & ENGINEERING DEPARTMENT
SCHOOL OF ENGINEERING
(213) 740-4339
tel: (213) 740 -1634
fax: -7797
internet: nutt@mizar.usc.edu

October 17, :994

To: Dr. R.C. Phohanka, Director, Materials Science and Tech. Division, Office of Naval Research

From: S.R. Nutt, Professor of Materials Science and Principal Investigator

Re: End-of-Fiscal-Year Summary

Contract Title: Creep Damage Mechanisms in Composites
Contract Number: N00014-91-J-1480
R&T Project Number:
ONR Scientific Officer: Dr. Steve Fishman

A. Research Goals

During the past year, research has focused on processing and characterization of intermetallic composites synthesized by plasma spray deposition. This versatile process allows rapid synthesis of a variety of different composite systems with potential applications for coatings, functionally gradient materials, rapid proto-typing and 3d printing, as well as near-net-shape processing of complex shapes. We have been pursuing an experimental program of research aimed at a fundamental understanding of the microstructural processes involved in the synthesis of intermetallic composites, including diffusion, heat transfer, grain boundary migration, and the dependence of these phenomena on deposition parameters. The work has been motivated by issues arising from composite materials manufacturing technologies. Recent progress is described in section B on the following topics:

i. Reactive atomization and deposition of intermetallic composites (Ni_3Al)
ii. Reactive synthesis of $MoSi_2$-SiC composites
iii. Mechanical alloying of nanocrystalline alloys
iv. Tensile creep deformation of BMAS glass-ceramic composites

'ome aspects of this work have involved collaboration with colleagues at the University of California. Irvine, nd at the United Technologies Research Center, East Hartford, CT.

ŀ. Significant Results

ʀeactive synthesis of plasma-sprayed $MoSi_2$-SiC composites

Molybdenum disilicide composites have been considered as potential high-temperature structural materials because of the combination of oxidation resistance and fracture toughness. One of the chief problems facing the development of these materials has been the existence of intergranular glassy films, which degrade the high-temperature properties. Reactive plasma spraying is a novel synthesis technique through which it may be possible to minimize the intergranular glassy films in these materials and achieve

higher volume fractions of SiC than are possible through more conventional processing routes, such as hot-pressing powder blends. In this process, the reinforcing phase is formed during synthesis by a reaction between a reactive gas (CH_4) and the molten droplets in the plasma. Of particular interest during the past year has been the issue of phase distribution within the microstructure. TEM methods employed to investigate this issue revealed a complex microstructure consisting of alternating layers of $MoSi_2$ and a two-phase mixture of Mo_5Si_3 and Mo_5Si_3C, as well as SiC inclusions situated at grain boundaries and prior droplet boundaries. The inclusions, which comprised 8% by volume, were effective in enhancing the fracture toughness (70-100%) and the resistance to creep deformation. The measured values of fracture toughness were superior to those typically reported for similar composites processed by P/M, XD, or self-propagating high-temperature synthesis. However, the mechanisms responsible for the enhanced toughness are presently unclear and require further investigation. Interestingly,, it appears that the SiC volume fractions obtained by reactive spray deposition are higher than those typically obtained by co-injection spray deposition. Higher volume fractions are believed to be possible by modifications to the process parameters.

Reactive atomization and deposition of intermetallic composites of Ni_3Al

Reactive atomization and deposition (RAD) is a modified plasma spray deposition technique that is being developed to synthesize dispersion-strengthened materials (composites). Atomization, in-situ reaction, and consolidation are combined into a single step by spray atomization and deposition with a reactive gas. The efforts of the past year have focused on synthesizing a Ni_3Al+Y+B alloy using a N_2-O_2 atomization gas and characterizing the resulting phase distribution to demonstrate the feasibility of this processing route. TEM observations revealed dispersoid phases of Y_2O_3, Al_3O_3, and $Y_3Al_5O_{12}$, as anticipated. The oxide dispersoids effectively pinned dislocations and grain boundaries that were apparently mobile during the deposition process because of the high-energy impact and semi-solid state of the droplets. Long-term annealing had little effect on the microstructure, an indication of the high thermal stability of the microstructure and resistance to grain growth derived from the dispersoids. The matrix was characterized by an unusual γ-γ' mosaic structure. The plate-like morphologies of the γ' phase may be beneficial to mechanical properties, including toughness, strength, and creep resistance. The important implications of the study are that the RAD processing method can be used effectively to synthesize oxide dispersion strengthened materials, and the spray deposition route is a cost-effective and versatile method of producing components in a variety of shapes.

Mechanical alloying of nanocrystalline alloys

Novel material properties can be obtained when the grain size approaches nanometer scale. A common way of achieving such structures is to rapidly solidify a molten metal (e.g. by melt spinning) to form a metallic glass, then ball mill the met-glass to form a nanocrystalline structure. A study was undertaken to develop an understanding of the mechanisms involved in the high-energy ball-milling process. An iron-boron-silicon Metglas alloy was cryogenically ball-milled, and the resulting powders were examined by TEM and characterized by thermal analysis. The TEM observations clearly showed nanocrystallites ~2nm in diameter of both α-Fe(Si) and Fe_2B in the cryomilled powders. During the early stages of ball-milling, the ribbon strips are bent by contact with the balls, causing localized deformation and shear bands. Subsequent sliding contacts together with impact events cause deformation and localized heating, leading to exolution of boron atoms from the iron lattice. (The equilibrium solubility of boron in iron is negligible.) Nanocrystals of Fe(Si) nucleate first, followed by Fe_2B crystallites. The kinetics for crystallization accelerate during the initial stages, then saturate as the volume of non-crystalline material diminishes. This results in a characteristic sigmoidal transformation curve, described by a Johnson-Mehl-Avrami relation. Future experiments will be undertaken to explore the effects of alloy additions, the atomic-scale mechanisms of crystal nucleation, and to fabricate nano-composites with novel properties.

Tensile creep deformation of BMAS glass-ceramic composites

The tensile properties of a glass-ceramic composite were investigated to determine the effectiveness of interface coatings designed to inhibit thermal oxidation, diffusion, and reaction and to enhance room-temperature toughness. A dual coating of SiC/BN was applied to the SiC fibers (CG Nicalon) by CVD prior to compositing. These materials have potential applications in turbine engine components. One of the critical challenges is to design an interface that is stable in oxidizing environments at high temperatures and also has the debond characteristics required for enhanced fracture toughness. In our recent work, the material retained tensile strength and modulus up to 1200°C, and during long-term creep experiments, the creep rates were negligible at 1100°C in air. However, creep at higher temperatures resulted in rapid failure and high creep rates. Fatigue experiments were conducted at high temperatures using stress levels just above the proportional limit stress. The material survived 10^5 cycles at 1200°C, although evidence of fiber degradation was observed microscopically. TEM observations of deformed samples showed that under most cases, the interface was stable, and even under severe conditions which produced damage, the damage occurred first in the fibers. Details of the reaction and chemical mechanisms are currently being studied.

C. Plans for next year

In the next phase of our research, we propose to continue work on several outstanding problems in this general area, as well as to pursue work on two new composite materials. Specifically, research is proposed on the following topics:

- interface damage during tensile creep of CMCs
- environmental effects on creep and fatigue behavior of CMCs
- long-term properties of Ti-SiC fiber composites
- oxidation-resistant interface designs for high-temperature CMCs
- melt-infiltration synthesis methods for Al-based MMCs

To assist in meeting these goals, acquisition of a new mechanical testing system is planned. This equipment, to be purchased with funds from an NSF award, will feature a controlled atmosphere chamber and high-temperature furnace, as well as a high-temperature strain gage, an oxygen gettering furnace, and an oxygen sensing system. The proposal has recently been funded, and plans are currently being made to purchase the equipment and locate it in newly renovated laboratory space.

Steven R. Nutt

S.R. Nutt, Principal Investigator

cc: S. Fishman, ONR Scientific Officer
C. Cometta, Engineering Executive Officer

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT
01 October 1993 through 30 September 1994

R&T Number:

Contract/Grant Title: Creep Damage Mechanisms in Composites

Scientifice Officer: Dr. S. G. Fishman

Principal Investigator: S.R. Nutt

Mailing Address: Materials Science Dept., University of Southern California, Los Angeles 90089-0241

Phone Number: (213) 740 - 1634

Fax Number: (213) 740 - 7797

E-mail address: nutt@usc.edu

a.	Number of papers submitted to refereed journals but not yet published	1
b.	Number of papers published in refereed journal (list attached)	3
c.	Number of books or chapters submitted but not yet published	0
d.	Number of books of chapters published (list attached)	0
e.	Number of printed technical reports & non-refereed papers (list attached)	2
f.	Number of patents filed	0
g.	Number of patents granted	0
h.	Number of invited presentations at workshops or professional meetings (list attached)	2
i.	Number of presenations at workshops or professional meetings (list attached)	2
j.	Honors/Awards/Prizes for Contract/Grant Employees)	1
k.	Providing the following information will assist with statistical purposes:	

PI:	Grad Students:	Post-Doctorals:
Total: 1	Total: 1	Total: 0
Female 0	Female: 0	Female: 0
Minority: 0	Minority: 0	Minority: 0

l.	Degrees granted (list attached)	0

D. LIST OF PUBLICATIONS/REPORTS/PATENTS/GRADUATES

1. Papers published in refereed journals (including those accepted for publication):

D.E. Lawrynowicz, J. Wolfenstine, E.J. Lavernia, S.R. Nutt, D.E. Bailey, A. Sickinger, and A.M. Hirt, "Reactive Synthesis and Characterization fo $MoSi_2/SiC$ Using Low-Pressure Plasma Deposition and 100% Methane," *Scipta Metall.* 31 (1994).

B. Huang, R.J. Perez, P.H. Crawford, A. Sharif, E.J. Lavernia, and S.R. Nutt, "Mechanically Induced Crystallization of Metglas $Fe78B_{13}Si_9$ During Cryogenic High Energy Ball Milling", *Scripta Metall.* **31** (1994).

X. Zeng, S.R. Nutt, and E.J. Lavernia, "Microstructural Characterization of Ni_3Al Processed by Reactive Atomization and Deposition", *Metall. Trans.* (1994).

2. Books or chapters of books published: (N/A)

3. Technical reports: (N/A)

4a. Invited presentations:

S.R. Nutt, ONR Workshop on Prevention of Environmental Degradation of Advanced Materials at High Temperaturs, University of Pennsylvania, March 1994.

S.R. Nutt. Pacific Coast Regional Meeting of the American Ceramic Society, Symposium on Emerging Characterization Techniques, Los Angeles, October 1994.

E.Y. Sun, J. Brennan, and S.R. Nutt, Deformation of Ceramics Meeting, Snowbird, Utah, August. 1994.

4b. Contributed presentations:

S. Nutt, "Two-Dimensional VLS Whisker Growth" Pacific Coast Regional Meeting of the American Ceramic Society, Los Angeles, October 1994.

S. Nutt, J. Brennan, and E.Y. Sun, "Control of Interfaces in Ceramic Composites", TMS Spring Meeting, San Francisco, CA, October 1993.

5. Patents granted (none)

6. Degrees granted (none)

E. Honors / Awards / Prizes

S.R. Nutt, awarded endowed chair, M.C. Gill Professorship in Composite Materials, USC, 1994.

G. Other sponsored research

Air Force Office of Scientific Research, "Interface Characterization in Glass-Ceramic Composites" (subcontract from UTRC), exp. 6-94, 1 mo. effort per year.

OFFICE OF THE UNDER SECRETARY OF DEFENSE (ACQUISITION)
DEFENSE TECHNICAL INFORMATION CENTER
CAMERON STATION
ALEXANDRIA, VIRGINIA 22304-6145

IN REPLY REFER TO DTIC-OCC

SUBJECT: Distribution Statements on Technical Documents

TO: OFFICE OF NAVAL RESEARCH
CORPORATE PROGRAMS DIVISION
ONR 353
800 NORTH QUINCY STREET
ARLINGTON, VA 22217-5660

1995 1027 028

1. Reference: DoD Directive 5230.24, Distribution Statements on Technical Documents, 18 Mar 87.

2. The Defense Technical Information Center received the enclosed report (referenced below) which is not marked in accordance with the above reference.

END-OF-FISCAL YEAR SUMMARY
N00014-91-J-1480
TITLE: CREEP DAMAGE MECHANISMS
IN COMPOSITES

3. We request the appropriate distribution statement be assigned and the report returned to DTIC within 5 working days.

4. Approved distribution statements are listed on the reverse of this letter. If you have any questions regarding these statements, call DTIC's Cataloging Branch, (703) 274-6837.

FOR THE ADMINISTRATOR:

1 Encl

GOPALAKRISHNAN NAIR
Chief, Cataloging Branch

FL-171
Jul 93

DISTRIBUTION STATEMENT A:

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION IS UNLIMITED

DISTRIBUTION STATEMENT B:

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES ONLY; (Indicate Reason and Date Below). OTHER REQUESTS FOR THIS DOCUMENT SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT C:

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES AND THEIR CONTRACTORS; (Indicate Reason and Date Below). OTHER REQUESTS FOR THIS DOCUMENT SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT D:

DISTRIBUTION AUTHORIZED TO DOD AND U.S. DOD CONTRACTORS ONLY; (Indicate Reason and Date Below). OTHER REQUESTS SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT E:

DISTRIBUTION AUTHORIZED TO DOD COMPONENTS ONLY; (Indicate Reason and Date Below). OTHER REQUESTS SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT F:

FURTHER DISSEMINATION ONLY AS DIRECTED BY (Indicate Controlling DoD Office and Date Below) or HIGHER DOD AUTHORITY.

DISTRIBUTION STATEMENT X:

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES AND PRIVATE INDIVIDUALS OR ENTERPRISES ELIGIBLE TO OBTAIN EXPORT-CONTROLLED TECHNICAL DATA IN ACCORDANCE WITH DOD DIRECTIVE 5230.25, WITHHOLDING OF UNCLASSIFIED TECHNICAL DATA FROM PUBLIC DISCLOSURE, 6 Nov 1984 (Indicate date of determination). CONTROLLING DOD OFFICE IS (Indicate Controlling DoD Office).

The cited documents has been reviewed by competent authority and the following distribution statement is hereby authorized.

A

(Statement)

OFFICE OF NAVAL RESEARCH
CORPORATE PROGRAMS DIVISION
ONR 353
800 NORTH QUINCY STREET
ARLINGTON, VA 22217-5660

(Controlling DoD Office Name)

(Reason)

(Controlling DoD Office Address, City, State, Zip)

Debra T. Hughes

DEBRA T. HUGHES
DEPUTY DIRECTOR
CORPORATE PROGRAMS OFFICE

(Signature & Typed Name)

(Assigning Office)

19 SEP 1995

(Date Statement Assigned)